

Photocross-linking of Low-Density Polyethylene.

I. Kinetics and Reaction Parameters

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SYNOPSIS

The kinetic characteristics and the reaction conditions of photocross-linking of low-density polyethylene (LDPE) in the melt have been studied using benzophenone (BP) and its derivatives such as 4-chlorobenzophenone (4-CBP) as photoinitiator and triallyl cyanurate (TAC) as cross-linker. The efficiency of the photoinitiated cross-linking system LDPE-BP-TAC and various factors affecting the cross-linking process, such as photoinitiator and cross-linker and their concentrations, irradiation time, temperature, and atmosphere, and UV light intensity were examined extensively by determining gel content, IR, and UV spectra. It has been found (i) that LDPE samples of 2–3 mm thickness are easily cross-linked to a gel content of about 70% with a UV-irradiation time of about 15 s under optimum conditions; (ii) that the photoinitiating system of a suitable initiator combined with a multifunctional cross-linker such as 4-CBP-TAC can enhance the efficiency of photocross-linking reactions, especially by increasing the initial rate of cross-linking; (iii) that photocross-linking of LDPE should be carried out in the melt, which increases the penetration of UV light by decreasing the scattering by crystallites, and (iv) that the rate of cross-linking is proportional to the square of the light intensity. An increase in light intensity can decrease the concentration of photoinitiator required to reach a certain rate of cross-linking. The photocross-linking of polyethylene is promising for industrial applications.

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INTRODUCTION

Both low-density and high-density cross-linked polyethylenes (XLPE) have become commonly used as industrial polymers in recent years. These products are extensively used for the electrical insulation of wires and cables, hot water piping, heat-shrinkable tubing, and film and as foam. Recently, there have been some major advances in the cross-linking of fibers.^{1,2} It is well known that a modest cross-linking of PE can considerably improve the thermal stability and the resistance to electrical discharge, solvent, creep, and environmental stress-cracking. Most commercial XLPE products to date are produced by two methods: high-energy irradiation (γ -

rays and electron beam)³ and chemical reaction (with peroxides⁴ and alkoxy silane⁵).

Photoinitiated cross-linking of PE by UV irradiation has been known since the 1950s when Oster and his co-workers⁶ first reported their studies. A number of experimental studies of photoinitiated cross-linking of PE were published in the following 30 years,^{7–11} but there has been no breakthrough in the commercial application of UV-cross-linking from these studies because of low penetration (< 1 mm thickness) and slow reactions (several minutes of UV irradiation required). The photocross-linking of PE has several inherent advantages, however, compared with the two commercial methods mentioned. For example, UV photocross-linking is highly efficient, there is little degradation or oxidation of the polymer during the UV cross-linking process, UV light sources are readily available and easy to handle, and the investment cost is low.¹²

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Recently, Rånby and co-workers¹³⁻¹⁷ developed a laboratory method for photocross-linking of PE in the melt. This paper is devoted mainly to studies of the kinetic characteristics and the reaction conditions of the photoinitiated cross-linking of low-density polyethylene (LDPE) and the various factors affecting the cross-linking process by determining gel content, IR, and UV spectra. By optimizing the reaction parameters, samples of LDPE, linear LDPE (LLDPE), and high-density polyethylene (HDPE) as thick as 2–3 mm are readily cross-linked within a UV-irradiation time of 15 s to a gel content of 70–90%. The main interest in the present work has been those types of cross-linked XLPE that can be used in the manufacture of electric wires and cables. Related studies of the mechanism of photoinitiated cross-linking and the properties and structure of photocross-linked XLPE will be presented in a series of forthcoming papers.

EXPERIMENTAL

Materials

The three kinds of polyethylenes used in the present work were branched LDPE and linear LDPE (LLDPE) from UNIFOS KEMI AB (now Neste Polyeten AB, Sweden) and HDPE Lupolen 5261z from BASF and Hostalen 412 from Hoechst AG. The symbols of the samples and some physical properties are listed in Table I.

Photoinitiators used were benzophenone (BP, mp 48.1°C, bp 306°C) (KEBO Lab, Sweden), 2-chlo-

robenzophenone (2-CBP, mp 52–56°C, bp 330°C) (Novakemi AB, Belgium), 4-chlorobenzophenone (4-CBP, mp 77–78°C, bp 332°C) (Fluka AG, Switzerland), and 4,4'-dichlorobenzophenone (4,4'-DCBP, mp 144–146°C) (Novakemi AB, Belgium). The cross-linking agents were triallyl cyanurate [TAC, C₃N₃(OCH₂CH=CH₂)₃] from Aldrich, Germany; trimethylpropane triacrylate [TMPTA, CH₃C(CH₂OCO—CH=CH₂)₃] from UCB, Belgium; and pentaerythritol tri-/tetra-allylether [PETAE, HOCH₂C(CH₂OCH₂CH=CH₂)₃/C(CH₂OCH₂CH=CH₂)₄] from Perstorp AB, Sweden.

Sample Preparation

All samples were mixed for 10 min at 160–200°C using a Brabender Plasticorder as 50 g batches of PE with the desired amounts of additives. After mixing, the samples were hot-pressed to sheets of suitable thickness for 5 min at 160°C for LDPE and LLDPE and at 180°C for HDPE using a Carver press. The sheet thickness was controlled by using frames of different standard thicknesses.

UV Irradiation

Samples were UV-irradiated in a UV-CURE device constructed in this laboratory, as shown in Figure 1. The UV lamp used was a Philips HPM 15, 2 or 1 kW, at a distance of 10 cm from the surface of the sample. The usual irradiation conditions of the samples were 4-CBP 1 wt %, TAC 1 wt %; irradiation temperature $T = 140^\circ\text{C}$ for LDPE and LLDPE and

Table I Commercial PEs and Their Properties

Symbol	Sample	Melt Index	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	ρ^a (g cm ⁻³)	T_m^b (°C)	Remark
LDPE							
A	DFDS 6600	0.2–0.3	4.3	—	0.924	115.0	
B	S-118975	2	3.2	—	0.922	112.0	
C	DFDS 47	2	3.2	—	0.922	112.0	With antioxidant Santonox 0.2%
LLDPE							
D	News 8572	2	3.2	—	—	—	With antioxidant
E	LLDPE 8016	—	—	—	—	126.0	
HDPE							
(L)	Lupolen 5261	1.0–2.3	2.7	8.7	0.950	—	
(H)	Hostalen 412	< 0.1	9.8	15.0	—	—	
F	L/H = 8/2				0.961	135.0	

^a As determined by the density gradient method.

^b As determined by the DSC method.

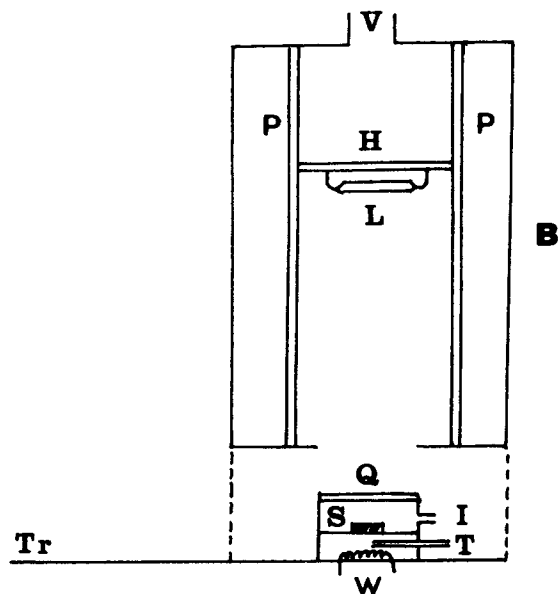


Figure 1 Schematic diagram of the irradiation device UV CURE: V, ventilation; P, stands; H, holder; L, lamp; Q, quartz plate; S, sample; I, N₂ entrance; Tr, track; B, shield box; W, heating wire; T, temperature detector.

150°C for HDPE; N₂ flow rate 1 L/min; HPM 15 lamp operated at 2 kW; and sample thickness 2 mm unless stated otherwise.

Analysis of Sample

Gel Content

After being irradiated, samples were cut into thin slices and put into a basket made of 200 mesh stainless-steel net. The gel content of XLPE samples was determined by extracting the irradiated samples (W_1) in the basket for 48 h with boiling xylene stabilized by 0.2% of antioxidant TINUVIN 144 and with N₂ bubbling to prevent oxidation. The solvent was renewed after the first 24 h of extraction. After the extraction, the basket was washed with acetone. After being dried in a vacuum desiccator at about 70°C to constant weight, the insoluble residue (W_2) was weighed. The average gel content (wt %) in the test was calculated as $100 (W_2/W_1)$. Usually, two or three samples were analyzed to determine the average gel content for a given set of irradiation conditions. This method of measuring gel content to study cross-linking has been shown to give reproducible results.^{9,12}

Ultraviolet and Infrared Spectra

UV absorption and IR spectra of polymer samples with additives were recorded using a Perkin-Elmer

575 UV/VIS spectrometer and a Perkin-Elmer FTIR 1700 computerized IR spectrometer, respectively.

RESULTS AND DISCUSSION

Characteristics of Photocross-linking

Gel formation is shown in Figure 2 as a function of irradiation time for samples of LDPE, LLDPE, and HDPE. It is evident that no cross-linking occurred for the PE resins without additives because no measurable gel was formed after irradiation for 160 s, but in the presence of 4-CBP and TAC (1 wt % each), there was a rapid increase in gel content with increasing irradiation time. Gel contents of about 70, 80, and 90% were obtained with irradiation time of 15 s for samples A, E, and F, respectively, as shown in Figure 2 (cf. Table I). It appears that the photoinitiating system of 4-CBP-TAC is very efficient. A suitable photoinitiator combined with multifunctional cross-linker can enhance the photocross-linking reactions considerably, as has been reported in detail in previous papers.¹⁴⁻¹⁷

The kinetic characteristics of cross-linking of the three PE samples had the same features: (i) the ini-

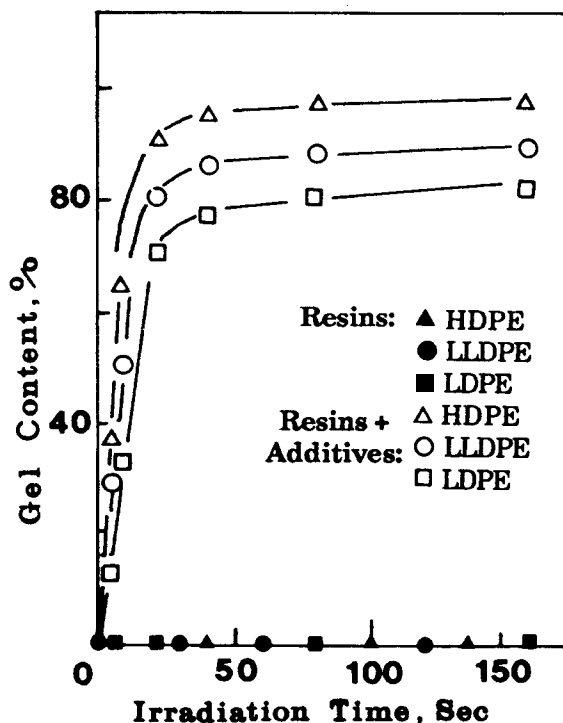


Figure 2 Kinetics of gel formation during photocross-linking of LDPE, LLDPE and HDPE in the melt. 4-CBP: 1 wt %; TAC: 1 wt %.

tial rate of cross-linking during the first 15 s was very fast; (ii) after 40 s, the rate decreased to a certain level, and (iii) the final gel content was almost constant. However, there are differences in the rates of cross-linking of the three PE types. Under the same conditions of irradiation, the order of rate of cross-linking and final gel content level are as follows:



The difference is interpreted as being due mainly to the different structures of the polymers, apart from the effects of molecular weight and molecular weight distribution. It has been reported^{18,19} that the radicals formed by irradiation decay considerably more quickly in branched PE than in linear PE. According to de Gennes' theory of diffusion,²⁰ the reptation motions of polymer chains are strongly suppressed by branching of the chains. This would explain why linear polyethylene (HDPE) cross-links at a higher rate and to a higher gel content than does branched polyethylene (LLDPE and LDPE).

Reaction Conditions

Effects of the reaction conditions such as concentration of photoinitiator and cross-linker, irradiation time, temperature, atmosphere, and light intensity on the photoinitiated cross-linking of PE have been studied.

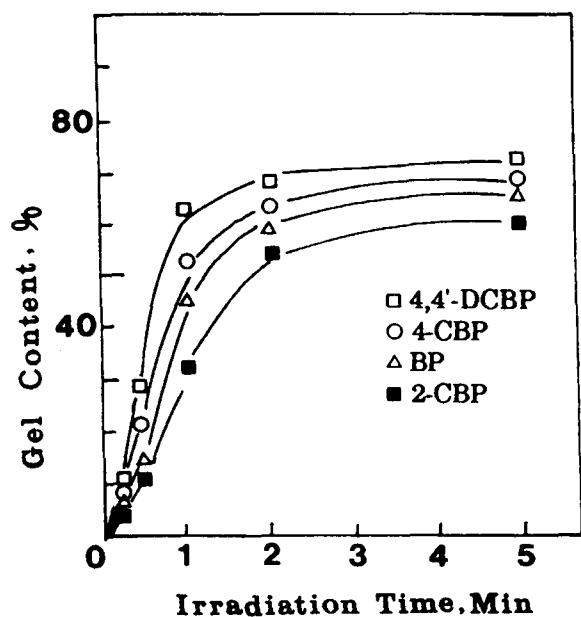


Figure 3 Comparison of the photocross-linking of LDPE with various initiators. Initiator: 1 wt %.

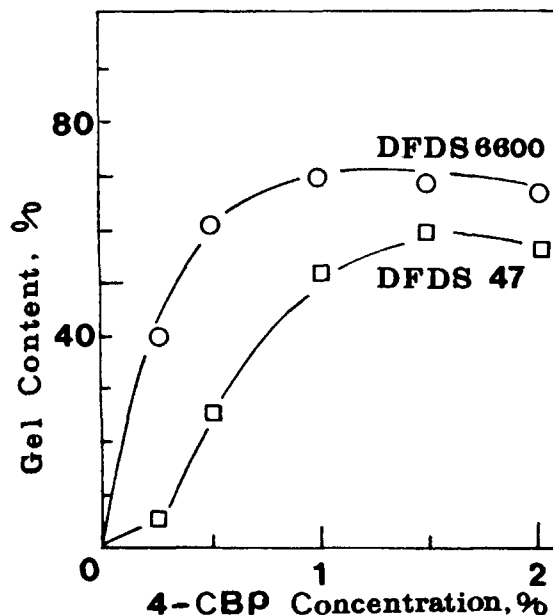


Figure 4 Effect of initiator concentration on photocross-linking of LDPE. TAC: 1 wt %; irradiation time: 30 s.

1. Photoinitiator

BP and its chlorine derivatives were found to be the most efficient of 18 photoinitiators tested in the photocross-linking of HDPE.¹⁶ Four initiators (BP, 2-CBP, 4-CBP, and 4,4'-DCBP) were selected and used in this work. Figure 3 compares their photoinitiating efficiency for sample DFDS 6600 with 1% by weight of initiator and no cross-linker added. Apparently, the photocross-linking behavior is similar for the four initiators, but the initial rates and final gel contents are different and decrease in the order



All the investigated samples show that 4,4'-DCBP is the most efficient initiator, which may be attributed to its good compatibility with PE, higher melting point, and lower volatility at the cross-linking temperature (140°C).

The data in Figure 4 show the dependence of gel content on the concentration of 4-CBP for the two LDPE samples DFDS 6600 (A) and DFDS 47 (C). The concentration of photoinitiator has a pronounced effect on the photocross-linking process, the optimum concentration of 4-CBP being about 1% by weight for these LDPE samples. At this concentration, the gel content has reached (sample A) or approaches (sample C) the maximum. A further increase in the amount of initiator does not increase

the final gel content. The samples A and C with 2% by weight of 4-CBP show an even lower gel content. The curves of photocross-linking as a function of photoinitiator concentration show an "autoretarding" phenomenon, which has also been observed by other authors.^{16,21,22} This is interpreted as being due to two effects: The BP in the ground state and the triplet state absorbs UV light in the region of $n-\pi$ transition that will screen the UV light and act as an "autoretardant." In addition, some of the ketyl radicals formed will combine with polymer radicals and prevent cross-linking. Some ketyl groups are retained in the cross-linked polymer. Both effects are expected to increase at higher BP concentration. The retardation of the initial rate of cross-linking and the low efficiency of the cross-linking in the case of sample C is interpreted as being due to the antioxidant added to the commercial resin sample.

2. Cross-linker

The addition of a multifunctional cross-linker greatly accelerates the cross-linking process, and the selection of a suitable cross-linker is very important. Figure 5 shows the efficiencies of three kinds of cross-linkers used with sample E. TAC is more efficient than are the others. It was found²³ that TAC with a cyanurate group has better solubility and is more homogeneously distributed in the EPDM rubbers than is PETAE or TMPTA. In addition, TAC promotes deeper penetration of cross-linking in

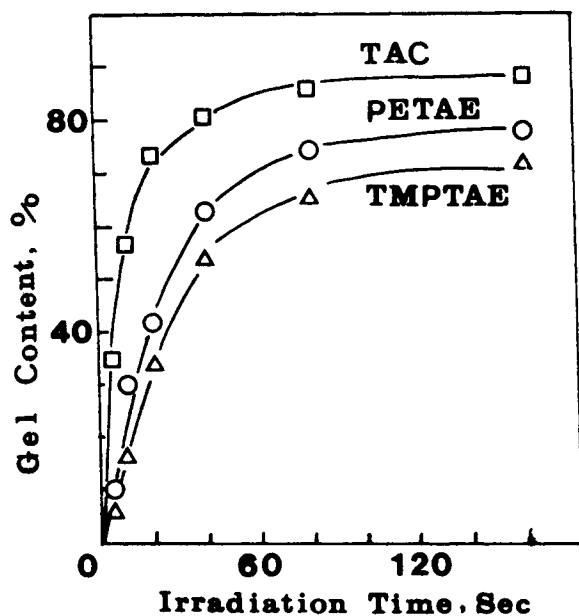


Figure 5 Effect of cross-linker on photocross-linking. Sample E: 4-CBP 1 wt %; cross-linker 1 wt %.

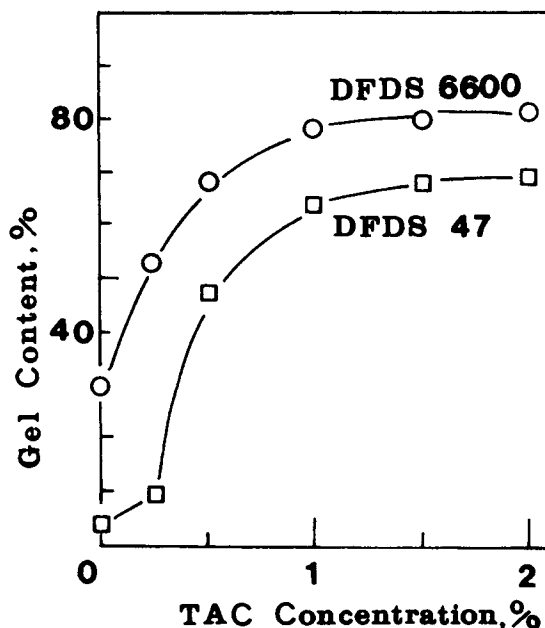


Figure 6 Effect of cross-linker concentration on photocross-linking. LDPE (A) and (C): 4-CBP, 1 wt %; irradiation time: 30 s.

XLPE^{15,16} and thus enhances the efficiency of photocross-linking.

The effect of TAC concentration on the gel content is shown in Figure 6. The results demonstrate that 1% TAC is an optimal amount for gel formation. Further addition of TAC has only a minor effect. In addition, residual amounts of cross-linker TAC remaining in XLPE decrease the photostability of the cross-linked LDPE, as pointed out by Wiedenmann.²⁴ An initial retardation is also observed in the case of sample C (DFDS 47) containing antioxidant (cf. Table I).

3. Irradiation Temperature

Figure 7 shows the effect of irradiation temperature on the gel formation for samples A and F. The results obtained for the LDPE (A) and HDPE (F) samples show different features. The LDPE exhibits a gradual change in gel content when it is irradiated near the melting point ($T_m = 115^\circ\text{C}$), whereas the HDPE exhibits a sudden change near T_m (135°C). This difference is interpreted as being due to the higher crystallinity of HDPE than of LDPE. Cross-linking of PE below the melting point is assumed to take place mainly in the amorphous regions.

4. Irradiation Atmosphere

The effects of irradiation atmosphere (N_2 , air, and O_2) on gel formation at a flow rate of 1 L/min

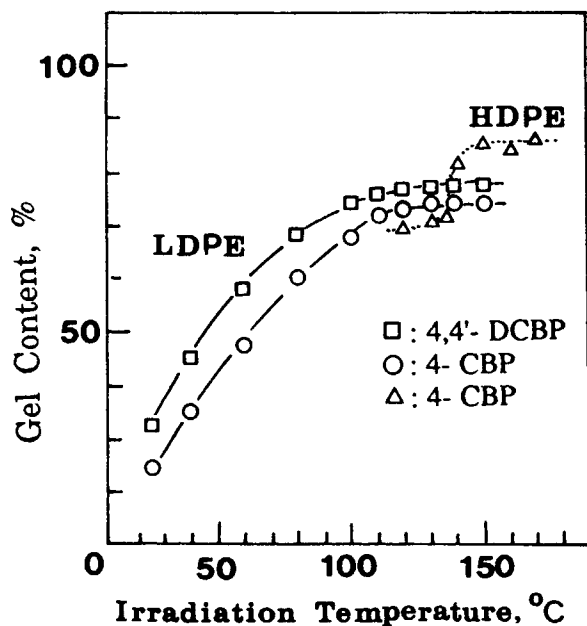


Figure 7 Influence of irradiation temperature on cross-linking rate for LDPE (A) and HDPE (F). Initiator: 1 wt %; TAC: 1 wt %.

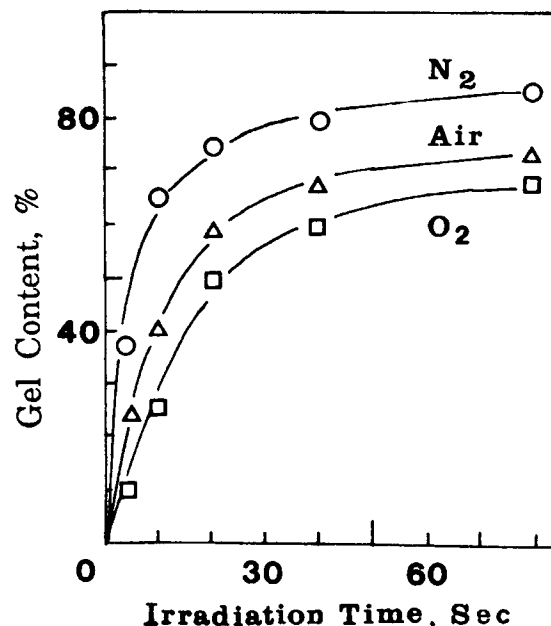


Figure 8 Influence of irradiation atmosphere on cross-linking rate of LDPE (A). 4-CBP: 1 wt %; TAC: 1 wt %.

through the reactor are shown in Figure 8. It is evident that oxygen suppresses the cross-linking process. The gel content of the sample irradiated in air is decreased by about 10%, and in O_2 , by about 20% compared with the sample irradiated in N_2 . Similar observations of the effect of oxygen on radiation cross-linking of polyethylene have been reported previously.^{9,14,25} The effect of oxygen on the photocross-linking of PE is due to the addition of oxygen to the radicals formed, which compete with cross-linking by radical combination. Because the solubility of oxygen in PE is low, the photochemical reaction of oxygen is controlled by its diffusion rate.²⁶ In the present case, thick samples and short irradiation times limit the penetration of oxygen into the interior of the sample. During irradiation, dissolved oxygen initially present is rapidly depleted and the diffusion of oxygen is too slow for efficient competition with the rate of cross-linking.

5. UV Intensity

The effect of UV radiation intensity on the rate of gel formation with increasing initiator concentration is shown in Figure 9. If we select 30% as a gel content of the initial step, it needs 2% initiator concentration with the 1 kW lamp, while it only needs 0.5% initiator with the 2 kW lamp at the same irradiation time for sample C with 0.2% antioxidant Santonex.

This means that the photoinitiating efficiency of the 2 kW lamp is four times that of a 1 kW lamp. Apparently, there is no severe screening effect at 2%

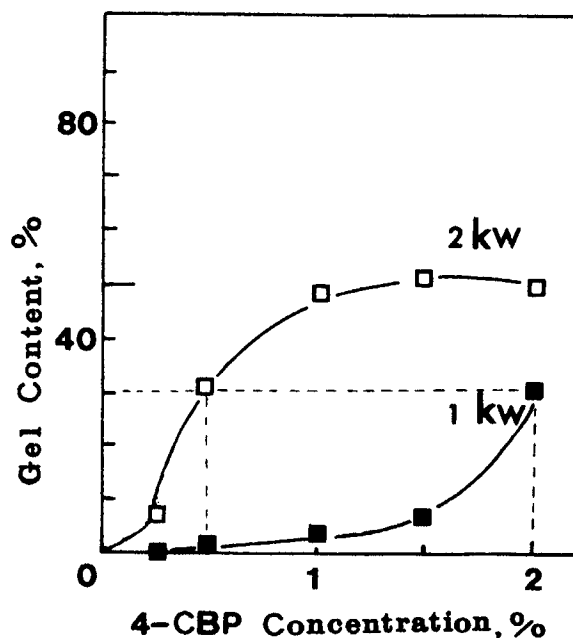


Figure 9 Effect of UV radiation intensity on the initial concentration of 4-CBP in LDPE (C). TAC: 1 wt %; irradiation time 30 s.

initiator concentration, i.e., the cross-linking rate is proportional to the square of the light intensity also for LDPE, as previously found for HDPE in the same cross-linking process.¹⁶ This interpretation is tentative because some chains react initially and are included in the network (the gel phase) at a later stage. The use of a high-power output lamp is important for attempts to increase the reaction rate of cross-linking in industrial applications.

Gel Formation Related to Photoinitiator Consumption

The influence of temperature on the photocross-linking process has been described previously (Fig. 7). A direct comparison of the cross-linking efficiency at room temperature (RT) and at the melt temperature has been made by observing IR absorption spectra for BP during cross-linking. The peak at 1667 cm^{-1} represents the IR absorption of the CO group in BP. The measurements are corrected for sample thickness using the internal standard peak at 1898 cm^{-1} for the C—H deformation modes in PE. The average for two or three samples is calculated. Figure 10 presents the relative absorbance A_{1667}/A_{1898} and the rate of gel formation with increasing irradiation time for samples cross-linked at room temperature and in the molten state (140°C). The consumption of BP in the reaction in

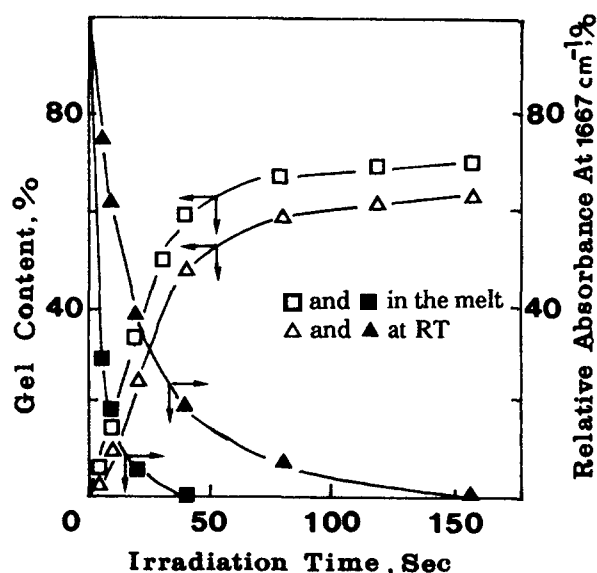


Figure 10 The rates of BP consumption and gel formation during photocross-linking of LLDPE sample (E). BP: 1 wt %.

the melt and the corresponding increase in gel content are much faster than at room temperature. The faster rate is due to better penetration of UV radiation and higher chain mobility in the melt than in the solid. The cross-links are formed by the combination of macromolecular radicals.

UV Absorption of Different Photoinitiators

The rates of cross-linking associated with four photoinitiators are given in Figure 3. The UV absorption spectra of the DFDS 6600 samples with 1% TAC and 1% photoinitiator (4,4'-DCBP and 4-CBP) and the emission spectrum from a Philips HMP 15 lamp are shown in Figure 11. The distribution of the emission intensity of the lamp mainly covers the 290–450 nm range. The UV spectra of photoinitiators show two main characteristic absorptions: One is a broad peak in the 310–400 nm region (the center at about 360 nm) attributed to a singlet (n, π^*) transition of the ketone group; another is a strong peak near 260 nm attributed to a singlet (π, π^*) transition of the same group. In view of the fact that (a) only a small tail portion of the $\pi-\pi^*$ absorption band of BP but the whole $n-\pi^*$ absorption band overlap the main emission region of the HPM 15 lamp and (b) that it has been proved²⁷ that the intersystem crossing of singlet (n, π^*) levels to triplet (10^{-12} s) is more efficient than that of singlet (π, π^*) levels to triplet (10^{-10} s), we suggest that 360 nm (n, π^*) absorption is of primary importance in the system investigated, i.e., photocross-linking of LDPE may be due mainly to the absorption of BP near 360 nm. The UV absorption of the photoinitiators compounded in the PE sample shows absorption in the same order as in solution.

CONCLUSION

Photocross-linking is an effective method of cross-linking LDPE, LLDPE, and HDPE. The photoinitiating system involving a suitable initiator combined with a multifunctional cross-linker such as 4-CBP-TAC can enhance photocross-linking reactions efficiently, especially by increasing the initial rate of cross-linking. The efficiency of photocross-linking of HDPE is higher than that of branched and linear LDPE under the same conditions.

Irradiation temperature and UV radiation intensity are of crucially important for increasing the rate of photocross-linking of thick PE sheets. Photo-

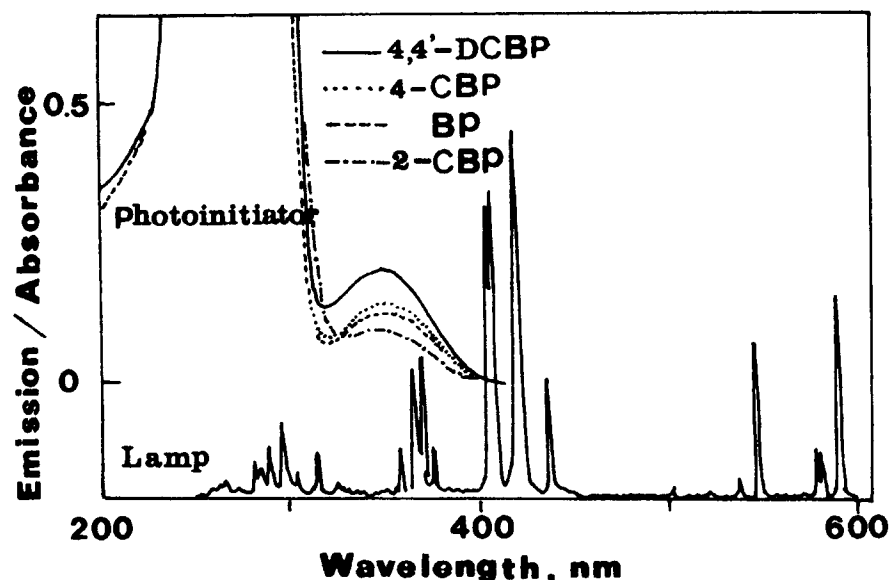


Figure 11 UV spectra of four photoinitiators ($4 \times 10^{-5} M$ in CHCl_3) and the relative emission spectrum from a Philips HPM 15 lamp.

cross-linking of PE should be carried out in the melt. The HPM 15 lamp of 2 kW has been preferred in the present work because the initial rate of photocross-linking is proportional to the square of the UV radiation intensity.

By optimizing reaction parameters such as the concentration of photoinitiator and cross-linker, irradiation time and atmosphere, and the selection of suitable resin, PE sheets as thick as 2–3 mm are readily cross-linked in the melt in short irradiation times (about 15 s) with a satisfactory degree of cross-linking (gel content: 70–90%). It is a very promising method for the industrial application of XLPE production. Recently, we developed industrial techniques of photocross-linking PE for the manufacture of cross-linked profiles, wire, and cable insulation.²⁸

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